Kinetics and mechanism of the hydrolysis of imidacloprid

Wei Zheng and Weiping Liu*

Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China

Abstract: The kinetics of the hydrolysis of imidacloprid were studied at different pH values and under various temperatures. Imidacloprid was found to be stable in acidic and neutral water, but readily hydrolysed in alkaline water. The main hydrolysis product was found to be 1-[(6-chloro-3-pyridinyl)methyl]-2-imidazolidone, and a mechanism for its formation is proposed.

Keywords: imidacloprid; hydrolysis; kinetics

1 INTRODUCTION

The hydrolysis of pesticides is an area that has received extensive study, since most compounds entering the environment will at some stage be in contact with water or be adsorbed in lipophilic media. It is also useful to understand hydrolysis pathways in order to determine the stability of the pesticide, to identify its hydrolysis products, and thus assess their toxicology, and to analyse residues.

Imidacloprid (Fig 1), 1-[(6-chloro-3-pyridinyl) methyl]-*N*-nitro-2-imidazolidinimine, is a new insecticide that possesses high potential activity against sucking pests.[1] It is effective for controlling various destructive insects, for example, leaf insects (aphids) and plant bugs (leaf hoppers).

Koester[2] investigated the metabolism of [^{14}C]-imidacloprid in plant cell suspension cultures. He found the main metabolites were 1-[(6-chloro-3-pyridinyl)methyl]-5-hydroxy-4,5-dihydro-*N*-nitro-1*H*-imidazol-2-amine and 1-[(6-chloro-3-pyridinyl) methyl]-*N*-nitro-1*H*-imidazol-2-amine, which might subsequently decompose to 6-chloronicotinic acid. The metabolism of imidacloprid in soil has been reported in relation to its use in sugar beet.[3,4]

Imidacloprid has been introduced to Chinese markets, replacing methamidophos and being widely used because of its high insecticidal effectiveness and low mammalian toxicity. In this paper, the kinetics of imidacloprid hydrolysis at different pH values and temperatures are described. The hydrolysis products were identified by HPLC, MS and IR, and a possible pathway for imidacloprid hydrolysis is proposed.

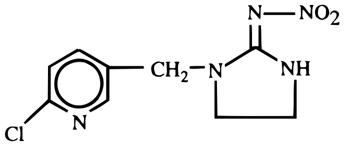

Figure 1. Structure of imidacloprid.

2 MATERIALS AND METHODS

2.1 Materials

Imidacloprid was supplied by Linhua Co (Zhejiang, China) with a chemical purity of 97.3%. Solubility in water was 0.51 mg litre^{-1}. Acetonitrile, methanol and chloroform were used as analytical grade solvents.

2.2 High performance liquid chromatographic analyses

A Spectra Physics liquid chromatograph equipped with a 250 × 4.6 mm id RP C_{18} analytical column, a multiwavelength Spectra 100UV-VIS detector and a workstation UPPER was used. The mobile phase (1 ml min^{-1}) was composed of acetonitrile + methanol + water (20, 20, 60 by volume) buffered with phosphate to pH 4. Under these conditions, the retention time of imidacloprid was 5.0 min.

2.3 Hydrolysis measurement

All glass apparatus was heat sterilized, and solutions were prepared in deionized water distilled from potassium permanganate. The hydrolytic rate was determined by monitoring the rate of disappearance of imidacloprid. Imidacloprid solutions of initial concentration 20 mg litre^{-1} were prepared at the

* Correspondence to: Weiping Liu, Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China
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required pH, using appropriate buffer solutions (according to the methods of Yang)[5] and sodium hydroxide. In order to restrain the growth of micro-organisms, 0.1 g sodium azide was added to each solution. The solutions were incubated in darkness with various conditions, 4-ml aliquots were removed at various times and the concentrations of imidacloprid and hydrolysis products were determined by HPLC.

2.4 Hydrolytic activation energy

Imidacloprid solutions (50 ml) of initial concentration 20 mg litre^{-1} containing 10 mM sodium hydroxide were incubated in darkness at six different temperatures (10,20,25,30,40,50°C). The batch hydrolysis curves were determined for each temperature, from which the activation energy was calculated.

2.5 Isolation of hydrolysis products

A flask containing a solution of imidacloprid (500 mg) in water (100 ml) containing a small amount of methanol was hydrolysed under alkaline condition (pH 12) at 20°C so that sufficient hydrolytic products could be obtained for isolation and identification. Small samples were removed at intervals, diluted, and examined by HPLC. Only one peak was observed in addition to that of imidacloprid. When HPLC analysis showed that imidacloprid was almost totally degraded, the solution was brought to pH 7.0 by the addition of 2 M hydrochloric acid, and extracted with ethyl acetate. The ethyl acetate layer was dried over anhydrous sodium sulfate and the solution was concentrated to dryness under vacuum. The hydrolysis product was recrystallized from hexane + dichloromethans (3 : 4 by volume).

2.6 Identification of hydrolysis product

The isolated hydrolysis product was identified by GC-MS, IR and HPLC.

HPLC analyses were carried out under the conditions described in Section 2.2. except that the mobile phase was acetonitrile + water (20 + 80 by volume).

GC-MS spectra were obtained with a Finnigan MATSSQ-700 Chromatograph-mass spectrometer equipped with a 30-m DB-5 column at 70 eV using electron impact ionization. The GC oven temperature was programmed as follows: isothermal at 50°C for 3 min; 50 to 300°C at the rate of 10°C min^{-1}; isothermal at 300°C for 8 min.

IR spectra were obtained with a Shimadzu IR-470 spectrometer. The samples were analyzed in potassium bromide pellets.

3 RESULTS AND DISCUSSION

3.1 Effect of pH on hydrolysis

Imidacloprid is only slowly hydrolysed in acidic and neutral waters (Fig 2). Only 1.5% of the initial content had been lost after three months at pH 7. Hydrolysis becomes more rapid under basic conditions, with 20% loss after three months at pH 9. The data for hydrolysis in alkaline solutions fit first-order kinetic equations (Fig 3). The equations and half-life values at pH 10.8 and pH 11.8 are given in Table 1.

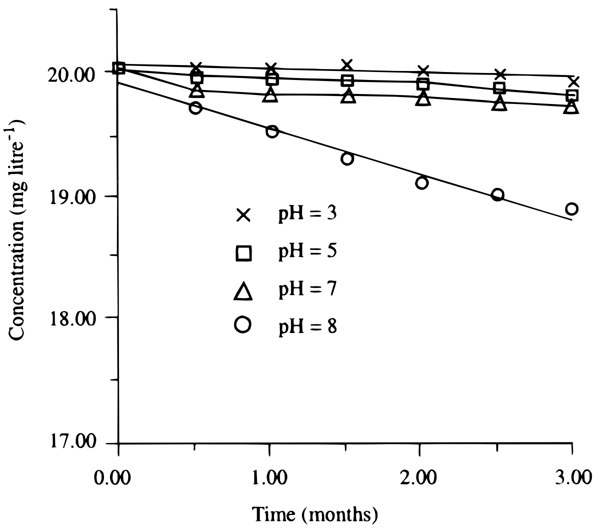

Figure 2. Hydrolysis of imidacloprid in acid and neutral solution.

3.2 Influence of hydrolysis temperature

The degradation curves for imidacloprid hydrolysis at different temperatures are shown in Fig 4. All the curves fit a first-order kinetic relationship. It can be seen also that the rate of hydrolysis is increased as the hydrolysis temperature increases. By applying the Arrhenius equation

$$\ln k = \frac{\mathrm{Ea}}{\mathrm{RT}} + \mathrm{B}$$

to the data, the activation energy for the hydrolysis of imadacloprid was found to be 42.72 kJ mol^{-1}.

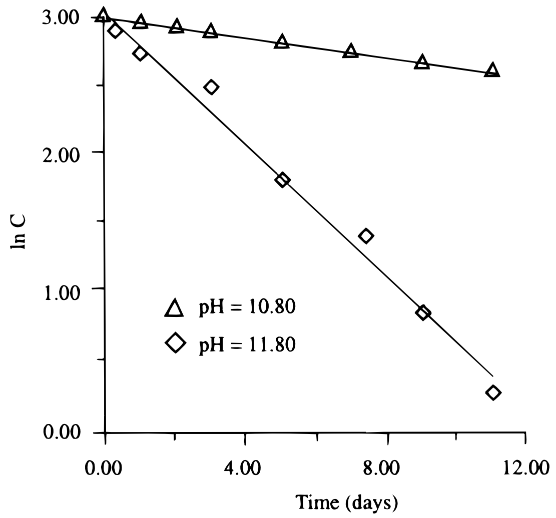

Figure 3. Kinetic curves of hydrolysis of imidacloprid in basic solution.

Table 1. Parameters for hydrolysis of Imidacloprid in aqueous solution

Hydrolysis equation $LnC = -kt + B$				
pH	*k*	*B*	R^2	$t_{0.5}$ *(days)*
10.8	0.035	3.02	0.996	20.0
11.8	0.243	2.93	0.990	2.85

3.3 Identification of hydrolysis products

3.3.1 *HPLC data*

The HPLC pattern of aqueous imidacloprid after hydrolysis showed only one peak apart from that for imidacloprid itself; the retention time of this compound was shorter than that of imidacloprid. No further hydrolysate peaks were observed during the subsequent complete degradation of imidacloprid, and the hydrolysate remained stable thereafter. It was concluded that there was only one main product of the hydrolysis of imidacloprid in basic media, and this was stable in alkaline solution and not easily decomposed.

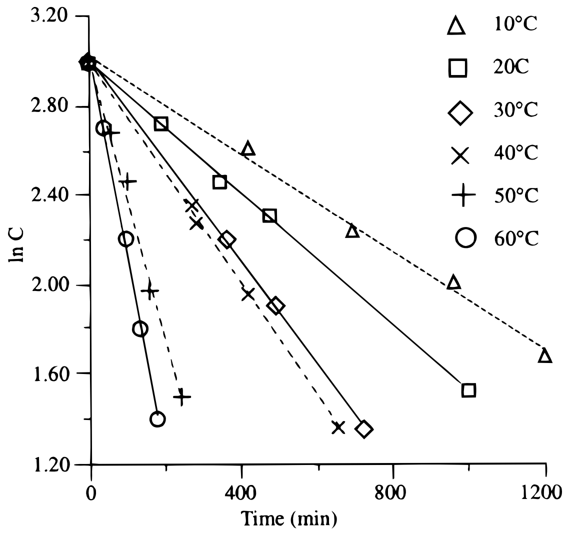

Figure 4. Hydrolysis of imidacloprid in 10 mM sodium hydroxide at different temperatures.

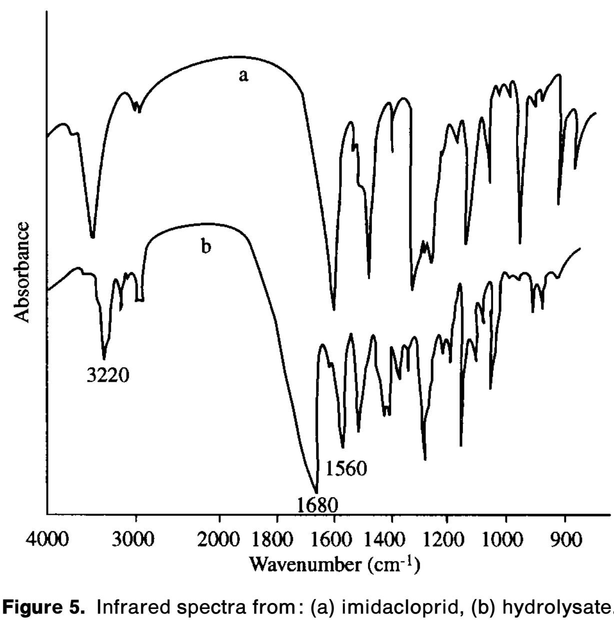

Figure 5. Infrared spectra from: (a) imidacloprid, (b) hydrolysate.

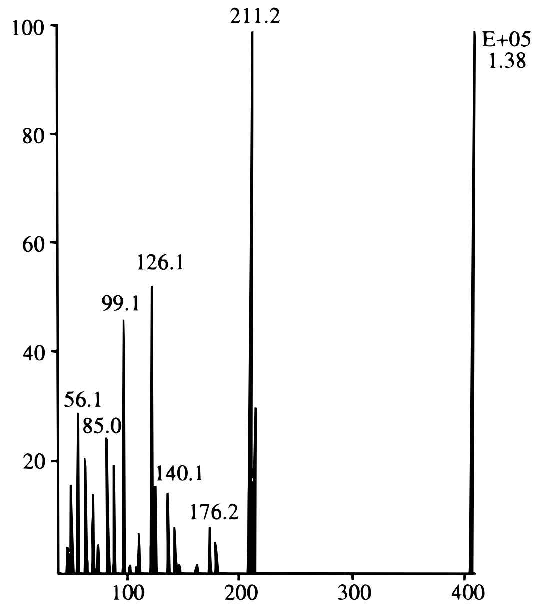

Figure 6. EI mass spectrum of hydrolysis product.

3.3.2 *IR spectra data*

When the IR spectrum obtained for the isolated hydrolysate was compared with that of imidacloprid, it could be seen (Fig 5) that the hydrolysate had a new sharp band at 1680 cm^{-1} due to C=O, along with $\nu_{N\text{-}H}$ (3220 cm^{-1}) and $\delta_{N\text{-}H}$(1560 cm^{-1}), indicating the presence of a -CO-NH- group.

3.3.3 *GC-MS spectra data*

The hydrolytic solution was assayed via GC-MS in electron impact (EI). By comparison of hydrolysed samples and a blank, the mass spectrum of the hydrolysate was obtained (Fig 6). By comparing the IR spectrum, HPLC retention time and MS spectrum of the isolated hydrolysate with those of an authentic standard, the hydrolysate was shown to be 1-[(6-chloro-3-pyridinyl)methyl]-2-imidazolidone. NMR and EA analyses also confirmed the proposed structure.

3.3.4 *Mechanism of imidacloprid hydrolysis*

From the structure of hydrolysate, we propose a possible imidacloprid hydrolytic pathway (Fig 7). Owing to the strong electron-withdrawing character of the NO_2 group, a small positive change (δ^+) is induced on the carbon of the C=N group of the imadazolidine ring, so that it is readily attacked by OH^-.

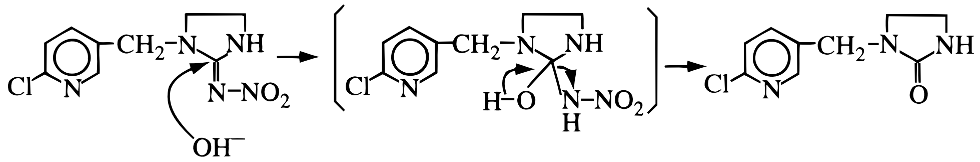

Figure 7. Proposed mechanism for hydrolysis of imidacloprid.

4. CONCLUSION

Little hydrolysis of imidacloprid occurs in acidic and neutral conditions. Under basic conditions hydrolysis of imidacloprid is highly pH- and temperature-dependent, high pH values and high temperature increasing the rate of hydrolysis. The hydrolysis of the pesticide gives only one main reaction product, 1-[(6-chloro-3-pridinyl)methyl]-2-imidazolidone.

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REFERENCES

1 Moriya K, Shibuya K, Hattori Y, Tsuboi S, Shiokawa K and Kagabu S, *Biosci Biotech Biochem* **56**:364–365 (1992).
2 Koester J, *Proc Brighton Crop Prot Conf*–Pests Dis **2**:901–906 (1992).
3 Rouchaud J, Gustin F and Wauters A, *Bull Environ Contam Toxicol* **56**:29–36 (1996).
4 Rouchaud J, Gustin F and Wauters A, *Bull Environ Contam Toxicol* **53**:344–350 (1994).
5 Yang K, *Huan Jing Hua Xue* (*China*) **13**:206–209 (1994).